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Title:

MOLYBDENUM DISILICIDE COMPOSITES FOR GLASS PROCESSING SENSORS

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MOLYBDENUM DISILICIDE COMPOSITES FOR GLASS PROCESSING SENSORS

DOE/OIT/GLASS INDUSTRY
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INTRODUCTION:

In October 1998, we initiated a Project funded by DOE/OIT/AIM/Glass Industry on "Molybdenum Disilicide Composites for Glass Processing Sensors". The objective of this Project is to develop strong, tough, thermal shock resistant, and molten glass corrosion resistant molybdenum disilicide ($MoSi_2$) composite tubes by plasma spray-forming techniques, that can be employed as protective high temperature sensor sheaths for a variety of advanced sensors and controls throughout the glass industry. The emphasis is on the development of advanced $MoSi_2$-Al_2O_3 coated, laminated, and functionally graded composite tubes. With Accutru International Corporation, we are developing silicide-based protective sheaths for self-verifying temperature sensors which may be used to accurately measure temperature in glass furnaces and other industrial applications. With Combustion Technology Inc., we are developing silicide-based periscope sight tubes for the direct observation of the surfaces of glass melts in glass furnaces. With Exotherm Corporation, we are characterizing combustion-synthesized silicide composite tubes.

PROJECT ACTIVITIES:

<u>Molten Glass Corrosion Tests on $MoSi_2$-Coated Al_2O_3 Thermocouple Protection Sheaths:</u>

Testing Performed at Thomson Consumer Electronics:

Funnel Glass:

A $MoSi_2$-coated Al_2O_3 thermocouple protection sheath was tested by Thomson Consumer Electronics (TCE) in their Funnel Glass. The sheath was immersed in the Funnel Glass for 16 hours at 1350 ^oC. The chemical composition of the Funnel Glass is (in wt.%): Al_2O_3: 3.25%; CaO: 3.42%; MgO: 2.35%; Na_2O: 6.62%; K_2O: 8.04%; PbO: 22.87%; Sb_2O_3: 0.20%; SiO_2: 53.25%.

The macroscopic appearance of the sheath after molten glass corrosion testing is shown in Figure 1a. There is very little corrosive loss of the $MoSi_2$ coating both above and below the glass line. Maximum corrosion has occurred at the glass line. Figure 1b shows the microstructure at the $MoSi_2$-glass interface. Phases present at the interface are primarily $MoSi_2$ and Mo_5Si_3. Wispy cloud-like features that were observed in the glass adjacent to the interface are shown in Figure 1c. X-ray analysis showed these wispy features to contain primarily silicon, with very little molybdenum present.

A thermodynamic analysis of the stability of $MoSi_2$ in the TCE Funnel Glass composition was performed using a commercially available HSC Chemistry for Windows software package (Outokumpu HSC Chemistry for Windows, 1999). In this analysis, 1 kg of $MoSi_2$ is allowed to come to thermodynamic equilibrium with a large amount (1000 kg) of the glass composition. The phases present and their amounts are then calculated by the software, based on a Gibbs free energy minimization rationale. These calculations were performed as a function of temperature.

Results of the thermodynamic calculations for the TCE Funnel Glass are shown in Figure 2. These results show that the $MoSi_2$ is very stable in the Funnel Glass up to a temperature of 1600 ^oC, where Mo_5Si_3 begins to form extensively, with minor formation of Mo_3Si and Mo.

These thermodynamic calculations are consistent with the macroscopic and microscopic observations of the $MoSi_2$-coated Al_2O_3 sheath, which indicated little or no reaction with the Funnel Glass. This result shows that $MoSi_2$ is stable in high lead molten glass compositions.

It is interesting to note that a slug of metallic lead was observed at the bottom of the Al_2O_3 crucible after the sheath corrosion test. Our thermodynamic equilibrium calculations have shown that this lead slug was not the result of any reactions of the molten glass with $MoSi_2$, but rather resulted from the instability of metallic lead in the TCE funnel glass composition in the range of 1100-1600 ^oC, as shown in Figure 3.

Panel Glass:

A $MoSi_2$-coated Al_2O_3 thermocouple protection sheath was tested by Thomson Consumer Electronics (TCE) in their Panel Glass. The sheath was immersed in the Panel Glass for 16 hours at 1350 ^oC. The chemical composition of the Panel Glass is (in wt.%): Al_2O_3: 2.20%; CaO: 2.65%; MgO: 0.06%; Na_2O: 8.26%; K_2O: 7.10%; SrO: 8.02%; BaO: 4.40%; TiO_2: 0.40%; Sb_2O_3: 0.30%; CeO_2: 0.26%; PbO: 3.32%; CoO: 0.00228%; NiO: 0.01874%; Cr_2O_3: 0.00101%; SiO_2: 63.01%. In comparing the TCE Panel Glass composition to the TCE Funnel Glass composition , the Panel Glass contains a larger number of chemical species and a lower concentration of lead oxide.

A macrophoto of the tested sheath is shown in Figure 4. Little reaction of the $MoSi_2$ with the Panel Glass occurred above the glass line and below the glass line. Maximum corrosion of the $MoSi_2$ is evident at the glass line.

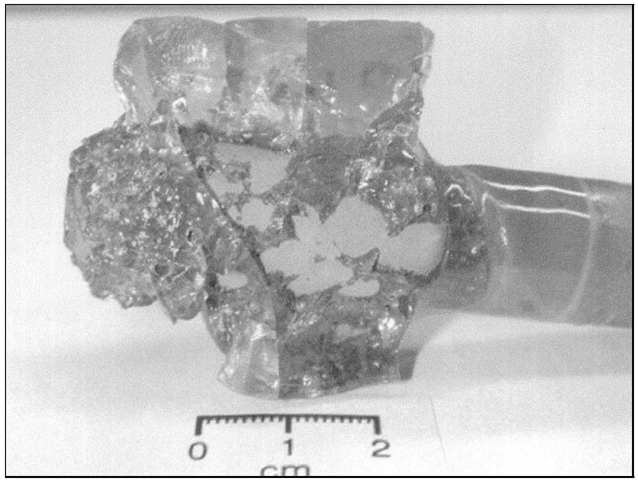
Results of the thermodynamic equilibrium analysis of $MoSi_2$ in the TCE Panel Glass are shown in Figure 5. $MoSi_2$ is thermodynamically stable in the Panel Glass composition to a temperature of approximately 1550 ^oC.

Testing Performed at Libby Owens Ford-Pilkington:

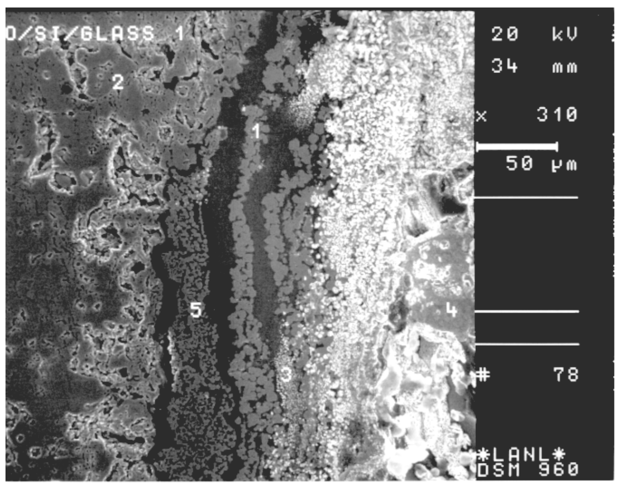
A $MoSi_2$-coated Al_2O_3 thermocouple protection sheath was tested by Libby Owens Ford (LOF)-Pilkington in their molten glass. The test was conducted for 72 hours at 1400 ^oC. The LOF-Pilkington glass composition (in wt.%) was: SiO_2: 72.2%; Na_2O: 13.5%; K_2O: 0.6%; MgO: 4.0%; CaO: 8.4%; Al_2O_3: 1.0%; Fe_2O_3: 0.12%; SO_3: 0.2%.

A macrophoto of the tested sheath is shown in Figure 6. The macrophoto only shows the area of the sheath that was below the glass line. Very little corrosion of the $MoSi_2$ was observed below the glass line. Maximum corrosion occurred at the glass line. The axial crack observed in the sheath was the result of a quench of the sheath into water after it was removed from the molten glass, which caused a thermal shock fracture.

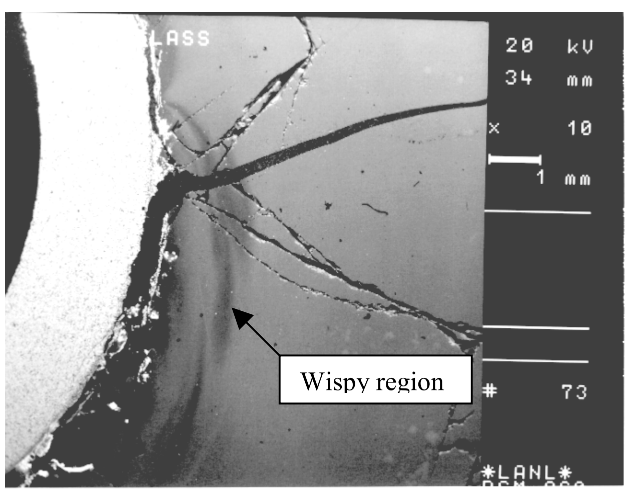
Equilibrium calculations of the stability of $MoSi_2$ in the molten LOF-Pilkington glass are shown in Figure 7. The equilibrium formation of a small amount of Mo_5Si_3 in this glass composition is observed for temperatures of 1000 ^oC and above.



(a) Macrophoto of corrosion tested $MoSi_2$-coated Al_2O_3 sheath



(b) Microphoto of $MoSi_2$-glass interface



(c) Wispy region in glass

Figure 1: $MoSi_2$-coated Al_2O_3 sheath after glass corrosion test in TCE Funnel Glass for 16 hours at 1350 ^oC.

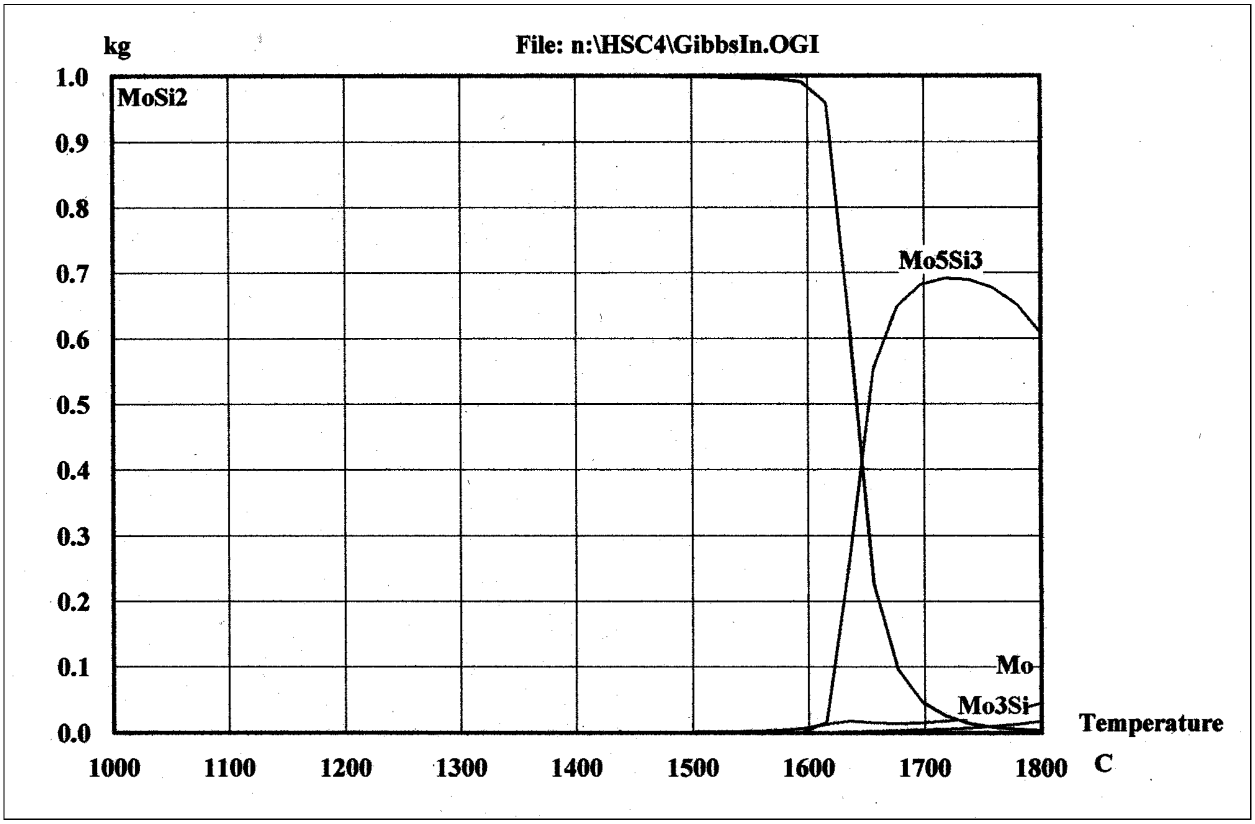


Figure 2: Thermodynamic analysis of equilibrium stability of $MoSi_2$ in TCE Funnel Glass composition, as a function of temperature.

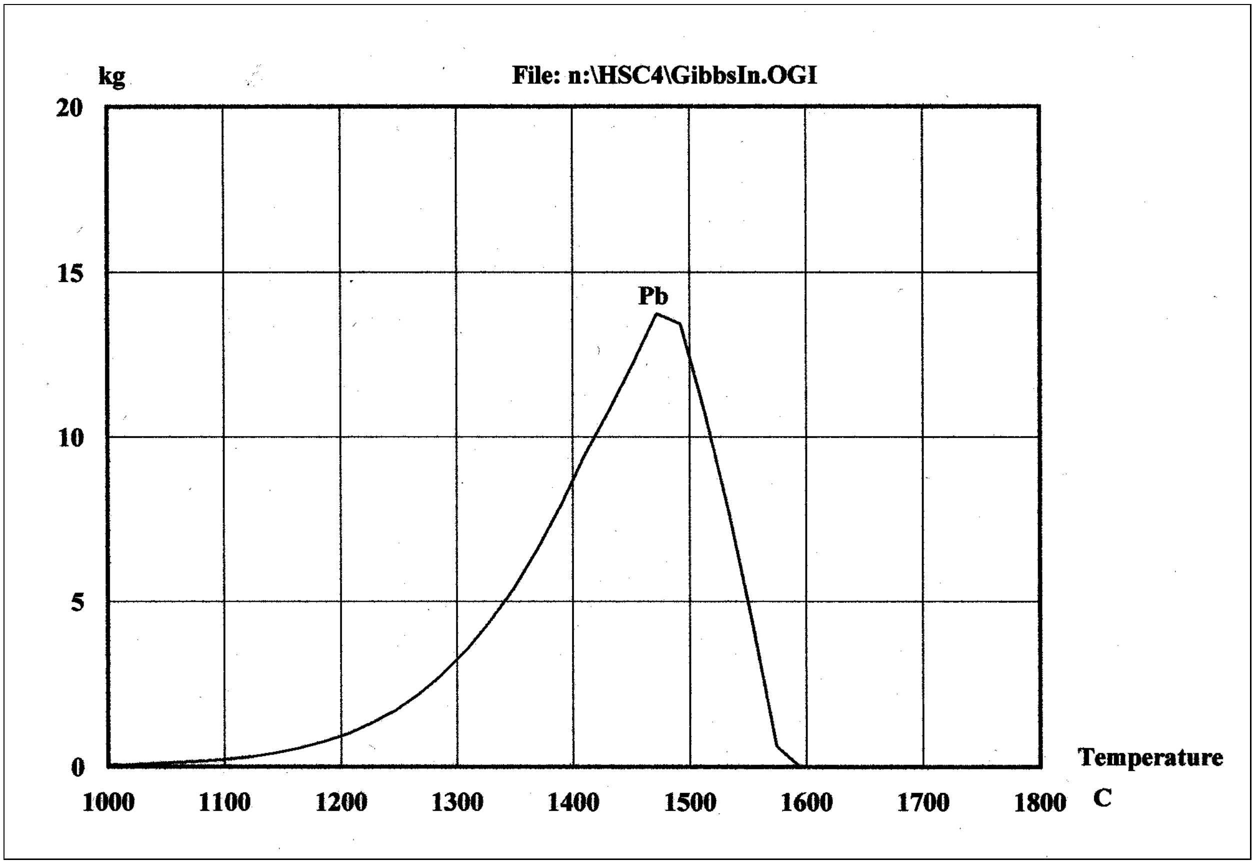


Figure 3: Thermodynamic stability of metallic lead in the TCE Funnel Glass. Significant quantities of metallic lead are stable in the temperature range of 1100-1600 ^{o}C in the Funnel Glass.

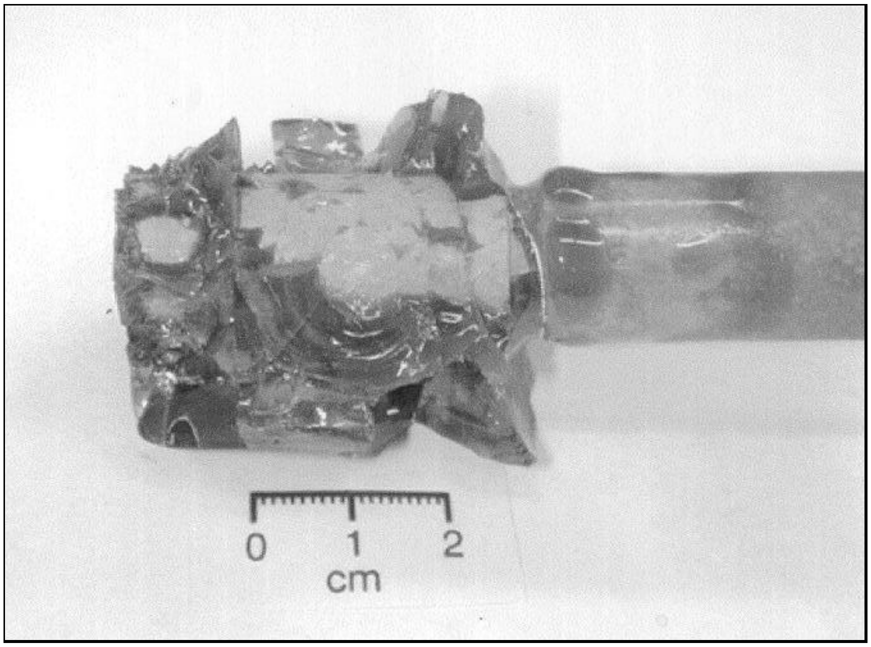


Figure 4: Macrophoto of $MoSi_2$-coated Al_2O_3 sheath after corrosion testing for 16 hours at 1350 ^{o}C in the TCE Panel Glass.

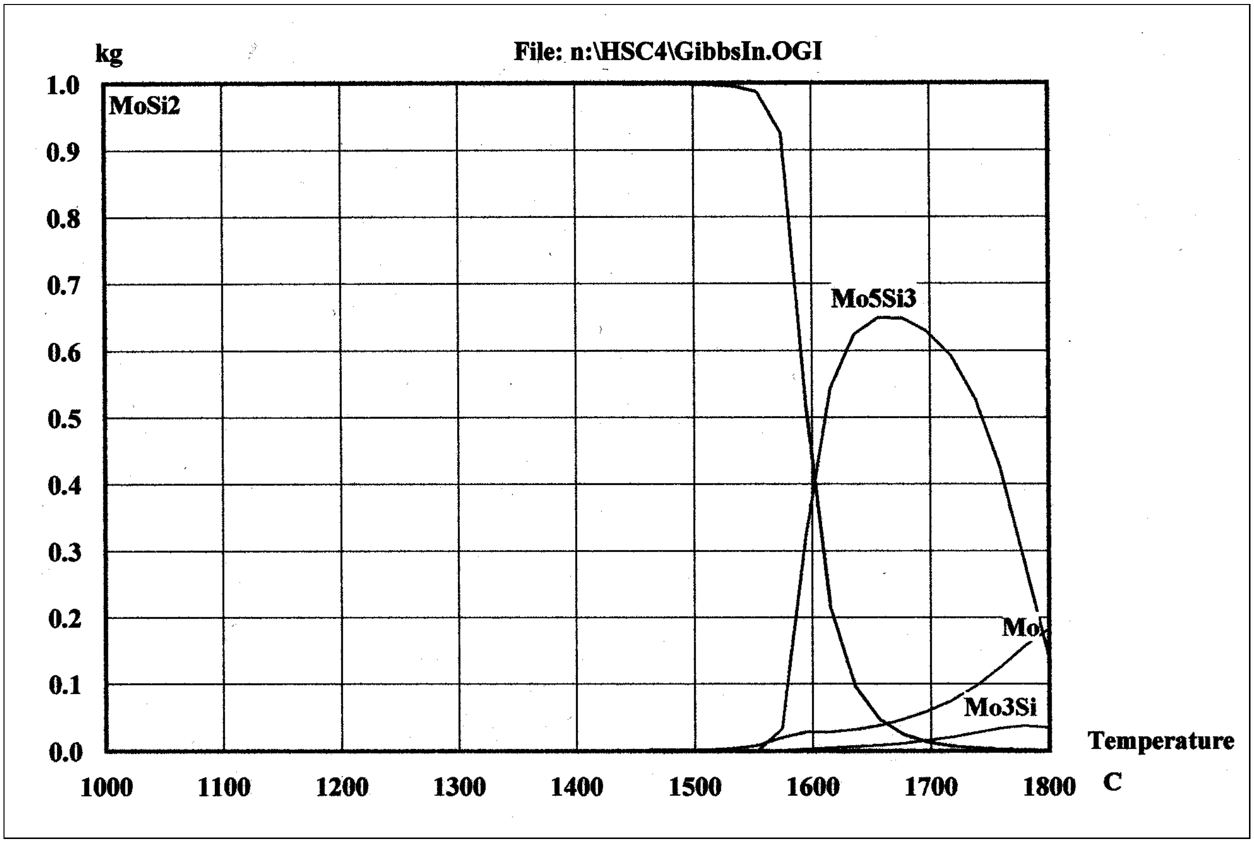


Figure 5: Thermodynamic analysis of equilibrium stability of $MoSi_2$ in TCE Panel Glass composition, as a function of temperature.

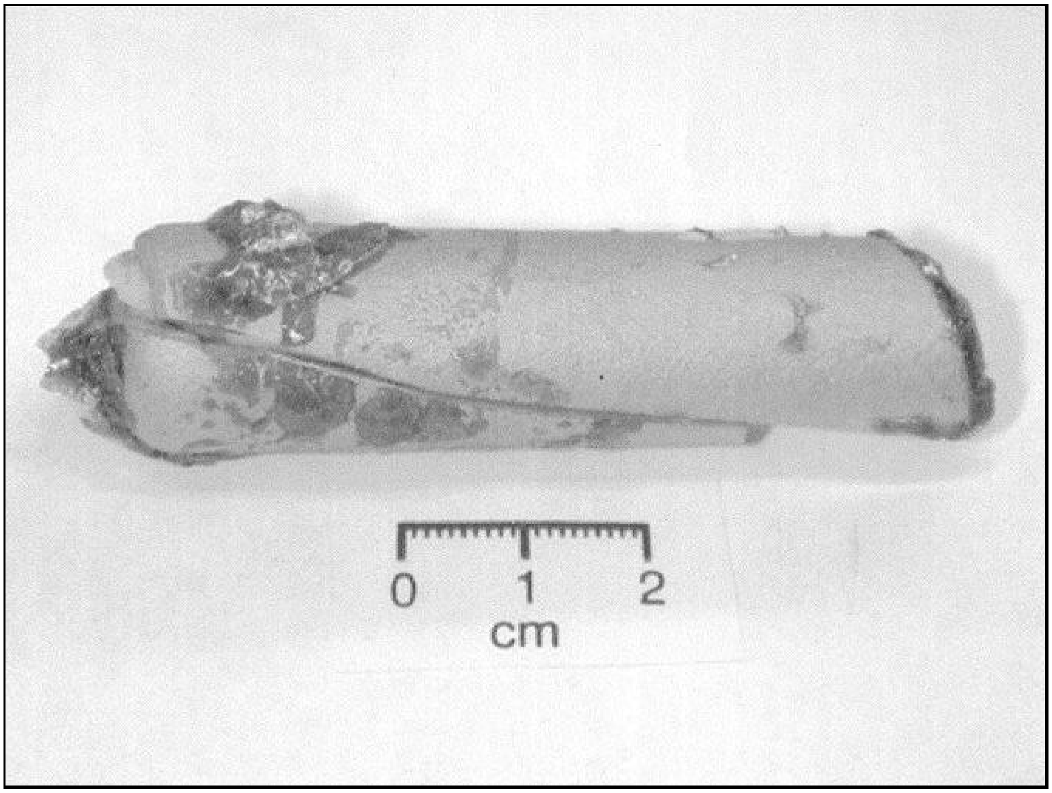


Figure 6: Macrophoto of $MoSi_2$-coated Al_2O_3 sheath after corrosion testing for 72 hours at 1400 ^oC in the LOF-Pilkington molten glass. Shown is the portion of the sheath that was below the glass line. The axial crack in the sheath occurred due to thermal shock when the sheath was quenched into water upon removal from the molten glass.

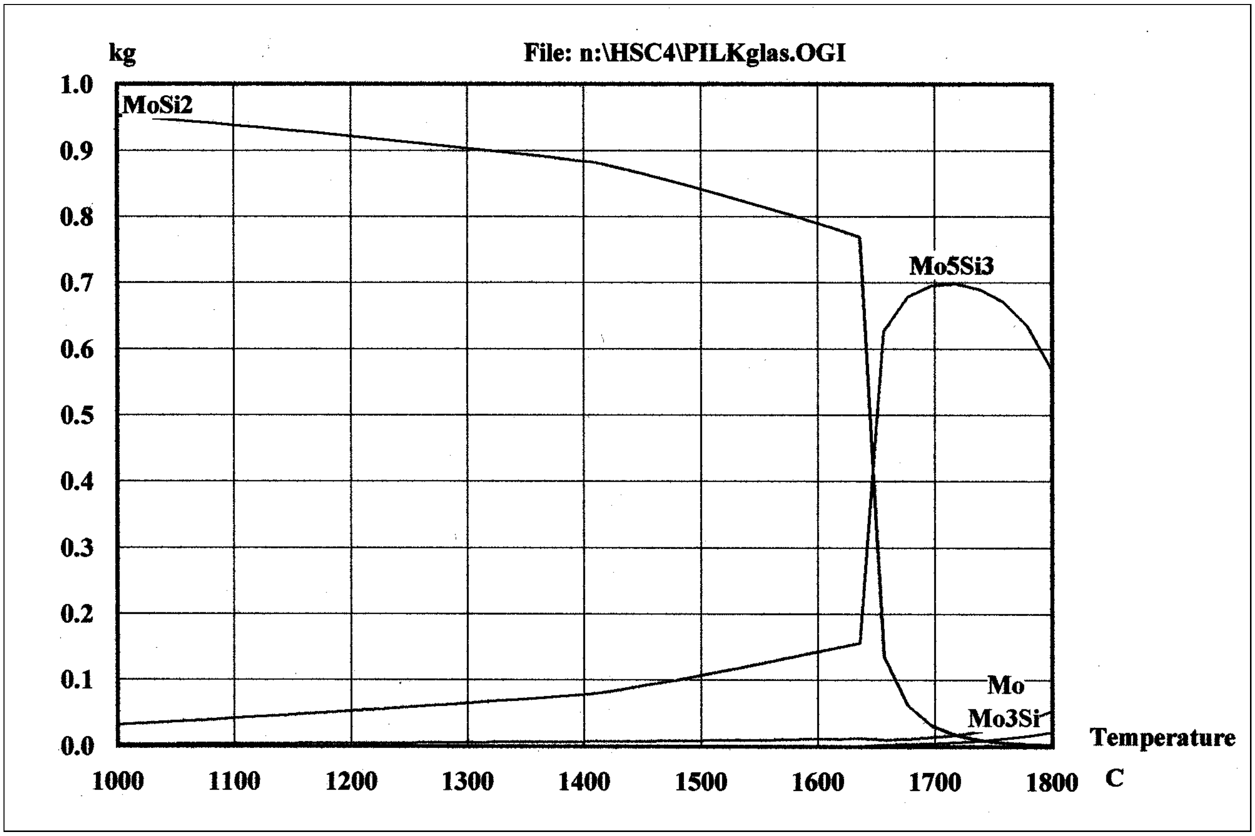


Figure 7: Thermodynamic equilibrium calculation of $MoSi_2$ in the LOF-Pilkington glass composition, as a function of temperature.